XAFS Study of Cr-doped Anatase

PNC-CAT

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Introduction

Diluted magnetic semiconductors (DMSs) couple free carrier conductivity in the host semiconductor to the ferromagnetic ordering of dopant ions distributed throughout the lattice to produce spin polarized currents. DMSs that exhibit spin polarized transport at and above room temperature are critically important to the development of spin electronics, or spintronics. Since the 1990s, considerable research effort has gone into understanding the growth and properties of magnetically doped III-V semiconductors, such as MnGaAs. As a result, significant progress has been made in understanding the nature of ferromagnetic ordering in these materials, and the relationship between magnetism and carrier spin polarization. However, the maximum Curie temperature seen to date is only 170 K.

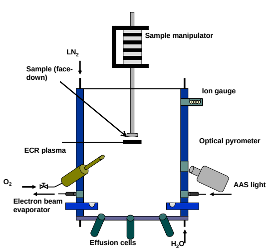
In 2001, Matsumoto *et al*. found that Co-doped anatase TiO2, a wide bandgap oxide semiconductor, was ferromagnetic at room temperature, leading to an explosion of research interest in doped transition metal oxides as potential DMS materials. However, the field has been marked by premature announcements of new high-Tc DMSs, based on poorly characterized materials. Magnetic contamination of substrates, magnetic secondary phase formation, and overall inadequate materials characterization has led to many “false starts” in the race to find new, robust DMSs.

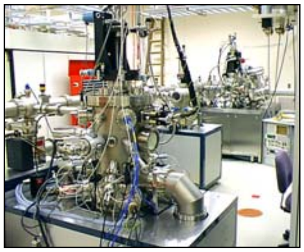
X-ray absorption measurements have been very useful in understanding these materials. Hard x-rays probe the entire film and can easily determine the valence and any residual metallic atoms that might be present. EXAFS can provide information about the lattice location of the metal dopant. This poster presents some recent work on Cr-doped TiO_2 anatase grown under different conditions (slow and fast) and on two different substrates (LAO and STO).

Why Cr doped Anatase?

Choosing anatase TiO_2 as the oxide host and Cr as the magnetic dopant is advantageous over other doped oxide systems for several reasons:

- When reduced, anatase has one of the highest electron mobilities of all the oxide semiconductors
- Chromium metal is antiferromagnetic; the presence of Cr(0) will not generate a spurious ferromagnetic signal
- The only potential ferromagnetic secondary phase is CrO_2, which is a half-metal in bulk with T_C slightly above room temperature (T_C = 386K)
- Theoretical calculations predict ferromagnetism in Cr-doped anatase
- High temperature ferromagnetism has been observed in Cr-doped AlN
- **Cr in anatase found to be ferromagnetic up to 690K**
  - See Doubay etal J. Appl. Phys. 97, 046103 (2005).





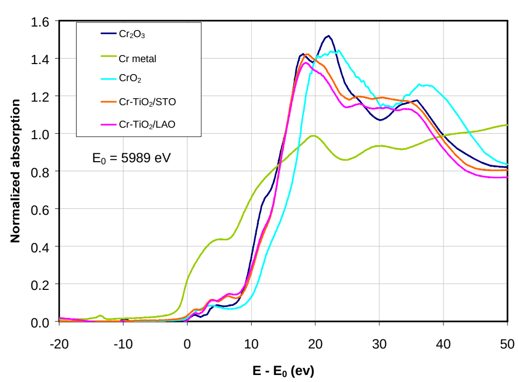
Thin films of Cr-doped anatase TiO_2 are deposited on lattice-matched $LaAlO_3$(001) (LAO, $\Delta a/a$ = -0.26%) and $SrTiO_3$(001) (STO, $\Delta a/a$ = -3.1%) substrates by oxygen-plasma-assisted molecular beam epitaxy. Films grown at 0.1 Å/sec showed nanoscale roughness while slow growth (0.015 Å/sec) gave smooth perfectly crystalline films.

X-ray measurements

The measurements were all made in fluorescence mode at beamline 20-ID and 20-BM. The samples were mounted on a spinner to eliminate Bragg peaks and oriented with the x-ray polarization parallel and perpendicular to the surface. The angle of incidence was 1-2 degrees. This angle is sufficient to minimize the substrate fluorescence while still probing the total film depth.

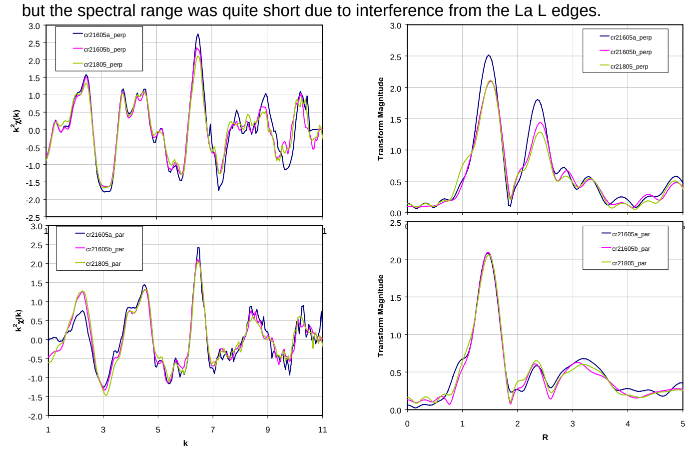
Near edge results

All of the near edge results were similar. The plot shows examples of the powder averaged data compared to some standards.
The valence looks similar to Cr3+, and there was no sign of any metallic Cr.



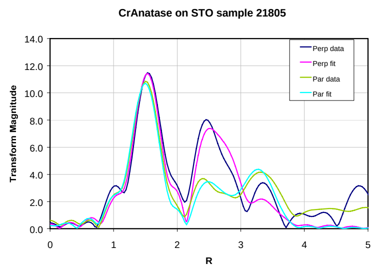
EXAFS results

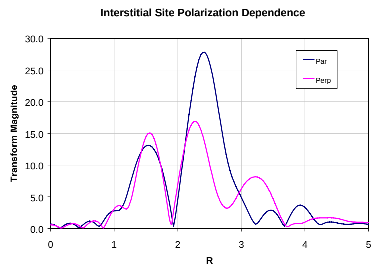
Below are the EXAFS results for three samples grown on STO for the two polarizations. Note the distinct polarization dependence of the higher shells. The data for samples on LAO looked similar, but the spectral range was quite short due to interference from the La L edges.



Fit to substitutional site model

Standard procedures were used to fit the spectra to FEFF7 models. The models were calibrated by fitting to Cr_2O_3. The fitting range is 2-10.5 in k and 1-3.8 in R. The two polarizations were fit simultaneously with a highly constrained model using only 14 parameters. The fit reproduces the polarization dependence well strongly confirming the substitutional site. For comparison the polarization dependence of a theoretical interstitial site is shown on the right. For the higher shells, it is opposite from the dependence in the data.





Detailed fitting results for the first shell

The first shell fitting results compared to an ideal anatase Ti site. Due to the relatively short data range N and sigma are correlated. If sigma is constrained to be similar to Cr2O3 (0.0038) then the N’s are quite close to the ideal values. In contrast to Co doping, there is no indication of O vacancies near Cr.

Sample	R perp	σ^2 perp	N perp	R par	σ^2 par	N par
Ideal TiO_2	1.966	-	2	1.937	-	4
21605A	1.96	0.0022	1.9	1.95	0.0015	3.7
21605B	1.98	0.0029	1.7	1.96	0.0028	3.9
21805	1.98	0.022	1.6	1.97	0.0039	4.2

The Cr atom is a good match to Ti, and the results indicate it is substituting with little distortion of the lattice. There is no evidence for significant interstitial site occupancy or vacancies in the Cr first shell.

Acknowledgements

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